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## (54) LAMINATES OF FOAMED POLYMERIC MATERIAL

(71) We, MOBIL OIL CORPORATION, a corporation organised and existing under the laws of the State of New York, United States of America, of 150 East 42nd Street, New York, New York 10017, United states of America do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to the manufacture of laminates of foamed polymeric material.

U.S. Patent 3,444,283 describes the production of foamed polymeric materials by heating and mixing a polymeric material such as polystyrene in the form of beads or pellets with a nucleating agent and a blowing agent prior to passing the heated mixture through a cooling zone and then an extruding die. The blowing agent is usually a gaseous material such as pentane, isopentane, butane, propane, hexane or petroleum ether, which is injected into the melt under high pressure. The nucleating agent is often referred to as a cell size control agent. It is added in amounts suitable for producing a foamed material of fine cell size, for example a cell size less than about 0.6 mm diameter. U.S. Patent 3,444,283 describes a cell size control agent comprising a mixture of a carbon dioxide liberating salt and an acid. The salt component may be any salt capable of reaction with an organic acid under standard extrusion conditions to liberate carbon dioxide. Examples of such salts include alkali and alkaline earth carbonates and bicarbonates of sodium, potassium, calcium, lithium, strontium and barium with sodium carbonate being preferred.

The acid component of the cell size control agent in U.S. 3,444, 283 comprises a mixture of two acids, one of which is in its hydrated form and the other in its anhydrous form. The two member acid components may consist of the same acid, for example, an organic acid which exists in both the hydrated and anhydrous

forms or they may be two different acids one being present as a hydrate and the other in its anhydrous form. Examples of organic acids which may be employed include oxalic, citric, succinic, itaconic, malonic, citraconic, adipic, malic, tartrac, phthalic, chloroacetic and diglycollic acids. Citric acid has been found to be most suitable to avoid undesired toxicity in food packagings.

The blowing agent often produces a plasticizing effect on the foamed polymeric material. When the foamed polymeric material is freshly extruded, it contains large quantities of residual blowing agent which produce a plasticizing effect. However, since the blowing agents are volatile, they escape from the polymeric material over a period of time, and because of this their plasticizing is fugitive. The plasticizing effect is particularly noticeable with blowing agents similar to pentane which are soluble in the polymeric material. Their plasticizing effect can be detected in the foamed polymeric material for a substantial period of time. On the other hand, the halo-carbon blowing agents such as "Freon" (trade mark) are less soluble in the polymeric materials and exert a smaller plasticizing effect which even then may be noticed in the foamed polymeric material after a substantial period of time.

We have found that the amount of nucleating agent used controls the density of an extruded foamed polymeric material. The density of the extruded material may approach the density of the unfoamed polymeric material. This control mechanism can be relied upon without causing undesired or significant change in the extrusion conditions, namely melt viscosity, pressure and temperature. For example, it has been found that the melt viscosity of the mixture with and without the nucleating agent is sufficiently similar to permit a process involving the co-extrusion of two or more streams of the same molten polymeric material but with different cell-forming

characteristics. these streams of similar viscoisty but different density-producing characteristics are co-extruded to a produce thermally-bonded, laminated sheet material varying considerably in density between the lamina. The foamed sheet which is produced by this method is a laminate of foamed polymeric material comprising at least two layers, each of a different density. The laminates may comprise for example, a core sheet of fine cell size bonded to polystyrene (of different cell size) on one or both sides. Thus, a surface sheet on one or both sides of a center, heat-insulating core material may differ considerably in cell size from the core and thus provide a surface of considerably different characteristics to the core.

According to the present invention there is provided a method of producing laminates comprising at least two layers of foamed polymeric material, the layers being of different densities, which comprises combining at an extrusion die, as herein defined, at least two streams of molten polymer composition containing a blowing agent and at least one of which streams contains an active nucleating agent, to form the laminate, at least one of the streams containing a smaller amount of active nucleating agent than the other stream or streams. The term "at an extrusion die" is used herein to mean that the streams are combined just before the die or in the die itself or that the streams are extruded through separate, but closely adjacent, die openings and are combined immediately outside the die lips. A plasticizing agent may optionally be present with the blowing agent.

The presence of the blowing agent is necessary to produce the desired foamed product. Also, it has the effect of plasticizing the molten polymer composition while it is in the extruder. We have found, for example, that unplasticized polystyrene is too viscous to flow through the die head at temperatures of about 140°C without the use of excessively high pressures. Thus, the blowing agent permits the use of normal foam extrusion conditions to produce a laminate product in which one (or more) of the layers resembles an unfoamed polymeric material.

The nucleating agent affects the cell size, as previously mentioned. However, we have found that by varying the amount of active nucleating agent in the polymer melt, the density of the product may be varied without affecting the flow characteristics of the melt. Thus, the normal foam extrusion conditions may be employed and this facilitates the extrusion with the layers of different density.

The properties of the extruded sheet vary considerably with the amount of nucleating agent, as shown by Table 1.

Table 1

## Comparison of Extruded Sheet Properties

Conditions:

Melt Temperature : 135°C

Extruded output : 68 Kg./hr.

Wt. % Nucleating Agent	Sheet Density (Kg/m <sup>3</sup> )	Sheet Thickness (mm)
0	480.5	0.25
0.56	72.08	2.5

In both of the above cases the same blowing agent was used, and in the same concentration.

From the above data it can be seen that the melt without any nucleating agent produced a high density product. The density of this extruded material approaches, in fact, the density of unfoamed polystyrene. This high density material therefore resembles unfoamed polystyrene in its properties. It can therefore be used to provide a layer which is impermeable to gas or liquid. This gas and liquid impermeable layer may be laminated, for example, on one or both sides of foam layer of low density which acts as a heat-insulating layer. The laminated sheet material may be used for making objects such as, for example, cups, plates, packing boxes and food container items requiring a liquid or gas impermeable surface adjacent an insulating surface. Thus, the laminated sheet material may be thermoformed into food packaging containers and other types of containers requiring, for example, a foamed thermoplastic material sandwiched between a liquid or gas impermeable surface material.

The different melt streams may be provided by blending different amounts of nucleating agent into separate streams of the polymer (before or after additions of the blowing agent) or, alternatively, a single melt stream containing a nucleating agent can be split into two or more separate streams and the nucleating agent in at least one of these streams can be wholly or partly deactivated. A suitable way of deactivating the nucleating agent is, in this case, by the application of heat. We have found that when a nucleating agent comprising a mixture of sodium carbonate and citric acid (preferably a mixture of hydrous and anhydrous citric acid, as previously mentioned) is heated to a suitably high temperature, generally from 260° to 290°C, its activity as a nucleating agent is destroyed. Thus, a melt containing the molten polymer, the blowing agent, sodium carbonate and citric acid (the sodium carbonate reacts with the citric acid to form sodium citrate) can be passed through a high temperature zone, such as an extruder barrel at about 290°C, to wholly or partly destroy the activity of the nucleating agent.

The present method is of particular utility in the production of polystyrene laminates as this polymer lends itself to foam extrusion

particularly well. However, other thermoplastic polymers may also be used.

Preferred embodiments of the method will now be described by way of illustration only, with reference to the accompanying drawings, in which:

Figure 1 is a diagrammatic illustration of an extrusion apparatus comprising a primary extruder and an auxiliary extruder feeding a coextrusion die, and

Figure 2 is a diagrammatic illustration of a coextrusion apparatus in which a heat-sensitive nucleating agent is used with the polymer charge to prepare two different types of melts which are passed to a coextrusion die.

In the extrusion apparatus of Figure 1, thermoplastic polymeric material mixed with nucleating agent is introduced through a hopper to a primary extruder 2 in which the mix is heated to a melt temperature in the range of 220° to 260°C. While it is being compressed it is combined with a gaseous blowing agent such as isopentane introduced by conduit 4 at a pressure within the range of 140 to 280 kg.cm<sup>-2</sup> but more usually at a pressure of 175 to 210 kg.cm<sup>-2</sup>. The mixture thus formed is then passed to a cooling section 6 of the extruder in which the temperature of the mix is reduced to a temperature in the range of 120° to 145°C. Cooling of the melt with the blowing agent in it is essential to provide a melt viscosity suitable for use in the extruder die 8. The higher the viscosity of the melt, the higher will be the pressure required for passing the melt through the extruder die. In the arrangement of Figure 1, a primary melt stream is passed by conduit 10 to an outer annular section 12 of die 8. It may, on the other hand, be passed to an inner annular section of the extruder die.

In the adjacent auxiliary extruder of Figure 1, a thermoplastic polymeric material is mixed with a predetermined amount of nucleating agent and introduced by hopper 14 in to the auxiliary extruder 16 in which it is heated to a melt temperature similar to that used in the primary extruder. The melt thus formed is then combined with pressurized blowing agent such as isopentane introduced by conduit 18 to form a pressurized melt of desired characteristics and similar to that developed in extruder 2. The introduction of the gaseous blowing agent considerably reduces the viscosity of the melt. Therefore the melt with gaseous blowing agent (and optionally with plasticizing agent) and a preselected amount of nucleating agent is then cooled in cooling zone 20 to provide a melt temperature similar to that obtained in cooling zone 6 of the primary extruder. The cooled material obtained from cooling zone 20 is passed by conduit 22 to the inner annulus 24 of die 8 before emerging as a co-extruded laminated material, under thermal bonding conditions through lip 26 of die 8, to form a thermally bonded laminate. The bubble 28 of

the extruded laminate passes over a cooling mandrel 30 before being split with cutting knives to form a flat sheet of laminate.

The coextruded thermoplastic materials vary in density as a function of the amount of nucleating agent used, and may also vary in thickness. The extruded materials may be foamed thermoplastic materials which vary considerably in density as a function of cell size. In the apparatus of Figure 1 heat-sensitive or insensitive nucleating agents may be employed and the amount of this material used in the auxiliary extruder may be varied over a considerable range to change the cell size and physical characteristics of the extruded melt. The isopentane or gas blowing agent functions as a plasticizing agent and it is relied upon, with temperature, to maintain a suitable melt viscosity for passage through the die at suitable die extrusion temperatures.

Melts of similar viscosity may be made with or without nucleating agent present in one of the melts and the separate melts so formed are at a sufficiently elevated temperature to bond upon contact with one another in the die annulus or when they leave it. The temperatures employed for bonding are adequate without undesirably disturbing the physical characteristics of the adjacently extruded thermoplastic material.

Figure 2 shows a modified apparatus. In the arrangement of Figure 2, a common primary extruder is used for forming a melt comprising thermoplastic material, nucleating agent and the blowing agent. A mixture of nucleating agent and thermoplastic material is introduced through hopper 32 into a primary extruder 34. In the primary extruder, the thermoplastic material is melted and mixed with nucleating agent and a blowing agent is introduced by conduit 36 to form a mixture at a pressure in the range of 140 to 280 kg.cm<sup>-2</sup> and at a temperature within the range of 200 to 260°C. The melt thus formed is then passed by conduit 38 to manifold 40 provided with valves 42 and 44. In this arrangement, a portion of the melt from the primary extruder passes by conduit 38 and 40 to a cooling extruder 46 which functions in a manner similar to that described above for zone 6 of Figure 1. In cooling extruder 46, the melt is cooled to a temperature which will produce a viscosity in the melt mixture suitable for extruding through a die to form the desired foamed sheet material (normally about 120±30°C). The cooled melt obtained from 46 is passed by conduit 48 to an inner annulus 50 of extruder die 52.

Another portion of the melt in conduit 38 is passed to a heating zone 54 followed by a cooling zone 56. In this arrangement, heating zone 54 is relied upon to heat the temperature of the melt to a temperature which will destroy the activity of the nucleating agent. The melt so produced, which contains no active nucleating agent will produce thermoplastic material

having a relatively larger cell size and a higher density than that portion of the melt containing active nucleating agent. In this case, the gaseous blowing agent functions also as a plasticizing agent or viscosity controlling agent. The material heated in zone 54 may then be cooled in an adjacent zone 56 to adjust the viscosity of the material to a value which is similar to the viscosity of the material in conduit 48. The temperature-adjusted material is then passed by conduit 58 to an outer annular space 60 circumscribing the inner annular space 50. The materials passed through annular spaces 50 and 60 merge under thermal bonding conditions adjacent the die lip. The bonding may be made to occur before or after the die lip is encountered. The coextruded material forms a bubble 62 of layered material when then passes over cooling mandrel 64 for further cooling and processing.

Alternately, a single stream of molten polymer can be divided into two or more separate streams and different amounts of nucleating agent added to each stream, although this would be less convenient.

#### WHAT WE CLAIM IS:

1. A method of producing laminates comprising at least two layers of foamed polymeric material, the layers being of different densities, which comprises combining at an extrusion die, as herein defined, at least two streams of molten polymer composition containing a blowing agent and at least one of which streams contains an active nucleating agent, to form the laminate, at least one of the streams containing a smaller amount of active nucleating agent than the other stream or streams.

2. A method according to claim 1 in which

the laminate comprises a layer of lower density foamed polymeric material laminated to a layer of higher density foamed polymeric material on one of its faces.

3. A method according to claim 1 in which the laminate comprises a layer of lower density foamed polymeric material laminated on both of its faces to layers of higher density foamed polymeric material.

4. A method according to any of claims 1 to 3 in which the polymeric material comprises polystyrene.

5. A method according to any of claims 1 to 4 in which a stream of the molten polymer composition blended with active nucleating agent is divided into two or more separate streams and the activity of the nucleating agent in at least one of the separate streams is reduced to provide a stream containing a smaller amount of active nucleating agent.

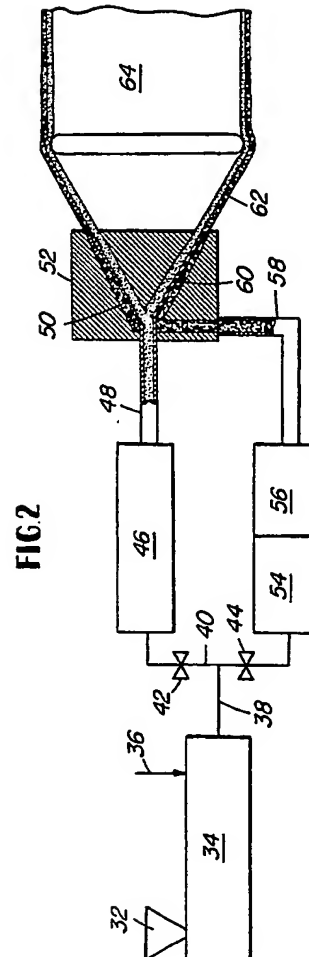
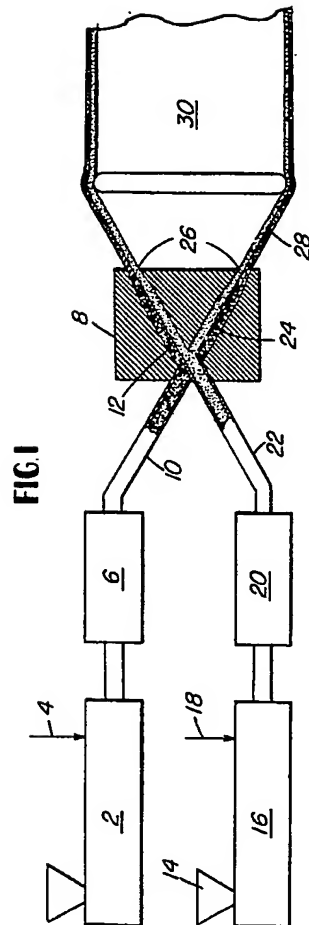
6. A method according to claim 5 in which the activity of the nucleating agent is reduced by heating the stream of polymer blended with nucleating agent.

7. A method according to claim 6 in which the nucleating agent comprises a mixture of sodium carbonate and citric acid.

8. A method of producing laminates of polystyrene substantially as herein described with reference to and as shown in Figures 1 or 2 of the accompanying drawings.

9. Laminates produced by a method claimed in any of claims 1 to 8.

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